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(71) Applicant: HITACHI MAXELL LTD

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(72) Inventor: NAGAI TATSU

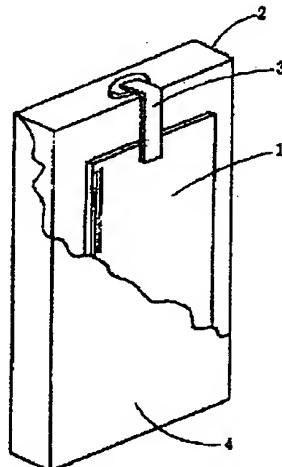
(54) HYBRID DEVICE CONSISTING OF ELECTRICAL
DOUBLE LAYER CAPACITOR AND BATTERY

(57) Abstract:

PROBLEM TO BE SOLVED: To provide an electric source in which a pulse discharge characteristic is excellent, especially at a low temperature.

SOLUTION: A hybrid device, in which an electrical double layer capacitor 1 and a battery 2 are combined and used as an electric source, is provided. A lithium secondary battery like a lithium ion secondary battery or a lithium polymer secondary battery is preferably used as the battery 2, and it is preferable that the electrical double layer capacitor 1 has a sheet shape and its thickness is in a range of 0.0025 X-0.15 X to an outer diameter (X) of a cylindrical battery, and within a range of 0.07 Y-0.3 Y to a thickness of a square shaped battery.

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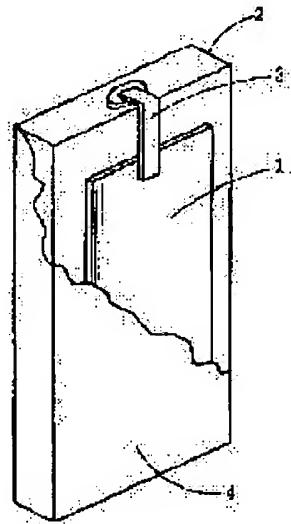
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LEGAL STATUS

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- [Date of final disposal for application]
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- [Date of registration]
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CLAIMS

[Claim(s)]

[Claim 1] The hybrid element of the electric double layer capacitor and cell which are characterized by combining an electric double layer capacitor and a cell.

[Claim 2] The hybrid element of the electric double layer capacitor and cell by which a cell according to claim 1 is characterized by being a rechargeable battery.

[Claim 3] The hybrid element of the electric double layer capacitor and cell according to claim 2 by which a rechargeable battery is characterized by being a rechargeable lithium-ion battery.

[Claim 4] The hybrid element of the electric double layer capacitor and cell according to claim 2 by which a rechargeable battery is characterized by being a lithium polymer rechargeable battery.

[Claim 5] The hybrid element of the electric double layer capacitor and cell according to claim 1, 2, 3, or 4 by which an electric double layer capacitor is characterized by the thickness being within the limits of $0.0025X-0.15X$ to the outer diameter (X) of a cylindrical shape cell by the shape of a sheet.

[Claim 6] The hybrid element of the electric double layer capacitor and cell according to claim 1, 2, 3, or 4 by which an electric double layer capacitor is characterized by the thickness being within the limits of $0.07Y-0.3Y$ to the thickness (Y) of a square shape cell by the shape of a sheet.

[Claim 7] The hybrid element of the electric double layer capacitor and cell according to claim 1, 2, 3, 4, 5, or 6 which are characterized by for the one side serving [the electric double layer capacitor] as the collecting electrode plate by the shape of a sheet, and for this one side contacting the outer wall of a cell directly, and making electric connection.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the hybrid element which a pulse discharge property, especially the pulse discharge property in low temperature can use as a good power supply in more detail about the hybrid element which consists of an electric double layer capacitor and a cell.

[0002]

[Description of the Prior Art] According to progress of pocket electronic equipment in recent years, the property required of a cell is becoming severe. For example, the device which uses a cell is miniaturized and a miniaturization is called for also for a cell in connection with it. On the other hand, elevation and the high current pulse usage of current value are increasing with multi-functionalization of a device, and digitization.

[0003] Until now, it has been coped with by coping with it by high-capacity-izing of primary cells, such as a manganese dry battery and an alkaline battery, improvement of a load characteristic, etc., or developing highly efficient rechargeable batteries, such as a nickel-cadmium battery, a nickel-hydrogen storing metal alloy cell, a rechargeable lithium-ion battery, and a lithium polymer rechargeable battery.

[0004] High capacity-ization of the capacitor used in order to back up memory apart from a main power supply on the other hand is also considered, and since an electric double layer capacitor is high capacity compared with a ceramic condenser, an aluminium electrolytic condenser, a tantalum electrolytic capacitor, etc., the thing using the electric double layer capacitor as a backup power supply is being put in practical use. Furthermore, the attempt which enlarges this electric double layer capacitor and is used as auxiliary power of the momentary output of an electric vehicle as a power capacitor is also made.

[0005]

[Problem(s) to be Solved by the Invention] Although the miniaturization of a cell and highly efficient-ization are demanded, high capacity and high power are performances which generally conflict, and it is difficult to make it compatible. For example, although, as for the alkali rechargeable battery which makes the electrolytic solution alkaline-water solutions, such as a nickel-hydrogen storing metal alloy cell and a nickel-cadmium battery, resistance of the electrolytic solution is obtained easily for a low reason, as for high power, high-energy density is hard to be obtained and hard to be called high capacity.

[0006] It is difficult to take out high power momentarily [since resistance of the electrolytic solution is high] on the other hand, although it can be made high-energy density, since the lithium polymer rechargeable battery using the latest lithium secondary battery, for example, a rechargeable lithium-ion battery, and the latest polymer electrolyte etc. can accumulate many energy. Property sufficient in especially the cellular phone as which property even with sufficient low temperature (-10 degrees C and -20 degrees C) is required cannot be demonstrated. Then, although adding a low-boiling point organic solvent and reducing the viscosity of the electrolytic solution is performed in order to improve this property, cell internal pressure will rise by addition of a low-boiling point solvent at the time of an elevated temperature, and safety will be missing.

[0007] this invention cancels the trouble of the above conventional technology, and aims at raising the pulse discharge property of lithium secondary batteries, such as a rechargeable battery especially a rechargeable lithium-ion battery, and a lithium polymer rechargeable battery, especially the pulse discharge property in low temperature.

[0008]

[Means for Solving the Problem] this invention unified the electric double layer capacitor and the cell as a hybrid element, and solved the above-mentioned technical problem by raising a pulse discharge property, especially the pulse discharge property in low temperature.

[0009] That is, by the cell with high internal resistance like a lithium secondary battery, it is thought by setting up the capacity of an electric double layer capacitor in consideration of pulse discharge time that equalization of a load becomes easy.

[0010]

[Embodiments of the Invention] In order to unite with a cell, as for the electric double layer capacitor which constitutes a hybrid element by combining with a cell as mentioned above, it is desirable that it is a sheet-like, and a flexible thing is desirable [a capacitor] so that it may be stuck and stuck on the periphery section to a cylindrical shape cell. Moreover, when a cell is a cylindrical shape cell, in order to obtain improvement in an effective load characteristic, as for the thickness of an electric double layer capacitor, it is desirable that it is within the limits of 0.0025X-0.15X to the outer diameter (X) of a cell. Namely, when the thickness of an electric double layer capacitor is within the limits of 0.0025X-0.15X to the outer diameter (X) of a cell Although

improvement in an effective pulse discharge property is obtained maintaining the same configuration without changing the outer diameter of a cell sharply since the electric double layer capacitor of a suitable capacity can be attached. If the capacity of an electric double layer capacitor becomes inadequate, or there is a possibility that the reliability of closure structure may fall, when the thickness of an electric double layer capacitor becomes thinner than the above-mentioned range, and the thickness of an electric double layer capacitor becomes thicker than the above-mentioned range. The whole volume becomes large too much, and although a pulse discharge property improves, a possibility that electric capacity may become small is considering volume. Furthermore, the charge collector of an electric double layer capacitor is a metal plate, and since structure can be simplified and a deployment of volume can also be performed by contacting the outer wall of a cell directly when serving as one of the two's structure for closure, it is desirable.

[0011] Although especially a flexible property is not required when a cell is a square shape cell, it is desirable that it is more desirable to become latus area thinly and it is a sheet-like like the above. Moreover, in order to obtain improvement in a suitable pulse discharge property, as for the thickness of an electric double layer capacitor, it is desirable that it is in the range of 0.07Y-0.3Y to the thickness (Y) of a cell. Namely, when the thickness of an electric double layer capacitor is within the limits of 0.07Y-0.3Y to the thickness (Y) of a cell. Although improvement in an effective pulse discharge property is obtained maintaining the same configuration without changing the thickness of a cell sharply since the electric double layer capacitor of a suitable capacity can be attached. If the capacity of an electric double layer capacitor becomes inadequate, or there is a possibility that the reliability of closure structure may fall, when the thickness of an electric double layer capacitor becomes thinner than the above-mentioned range, and the thickness of an electric double layer capacitor becomes thicker than the above-mentioned range. The whole volume becomes large too much, and although a pulse discharge property improves, a possibility that electric capacity may become small is considering volume.

[0012]

[Example] Below, an example is given and this invention is explained more concretely. However, this invention is not limited to those examples.

[0013] Two electric double layer capacitors shown in drawing 1 were produced by making them into a sheathing material using the aluminum plate of the shape of a rectangle whose dimension is 32mmx46mm by 0.25mm in example 1 thickness.

[0014] It consists of activated carbon fiber of the shape of a rectangle whose dimension thickness is 0.3mm and is 28mmx42mm, and a negative electrode 12 is also 0.3mm and, as for the positive electrode 11, thickness consists of [the negative electrode] activated carbon fiber of the shape of a rectangle which is 28mmx42mm for the dimension. Separator 13 consists of a polypropylene nonwoven fabric, and is arranged between the above-mentioned positive electrode 1 and the negative electrode 2.

[0015] The electrolytic solution becomes propylene carbonate from what carried out 1 mol/l dissolution of the 4-ethylammonium truffe RUORO borate (Et4 N-BF4), the aforementioned positive electrode 11, a negative electrode 12, the separator 13 also including this electrolytic solution, etc. are held in the space surrounded with the collecting electrode plate 14 for positive electrodes, the collecting electrode plate 15 for negative electrodes, and the frame 16, those planes of composition are sealed with adhesives, and the electrolytic solution is made not to be leaked outside.

[0016] The collecting electrode plate 14 for positive electrodes and the collecting electrode plate 15 for negative electrodes consist of an aluminum plate with a thickness of 0.25mm as mentioned above, a frame 16 is a product made from a polyethylene terephthalate, and the thickness of this whole electric double layer capacitor is 1.4mm.

[0017] On the other hand, as a cell, thickness connected the collecting electrode plate 14 for positive electrodes of the electric double layer capacitor 1, and the positive-electrode terminal of a cell 2 with the lead object 3 made from nickel using the square shape rechargeable lithium-ion battery whose dimension is 34mmx48mm by 8mm, covered with the sheathing material 4 made from a polyvinyl chloride except for a part for a terminal area, and produced the hybrid element shown in drawing 2.

[0018] Open circuit voltage is 3.6V and the theoretical electric capacity of the above-mentioned cell 2 is 850mAh(s). It is the square shape rechargeable lithium-ion battery of well-known composition of having used the artificial graphite for the negative electrode as an active material in the positive electrode, using a lithium cobalt oxide as an active material. Since the thickness (Y) of this cell 2 is 8mm, the thickness (1.4mm) of the above-mentioned electric double layer capacitor 1 is within the limits of 0.07Y-0.3Y (0.56mm - 2.4mm) to the thickness (Y= 8mm) of a cell 2. Moreover, although not shown in this drawing 2, the collecting electrode plate 15 for negative electrodes of the electric double layer capacitor 1 and the cell case which constitutes the negative-electrode terminal of a cell 2 are connected with the lead object made from nickel. The pulse discharge property in cellular-phone mode was investigated so that it considered as a power supply after charging this hybrid element completely, and it might be shown after that, using as the power supply for comparison the cell shown in the after-mentioned example 1 of comparison.

[0019] By 3.6V, the same open circuit voltage as the square shape rechargeable lithium-ion battery used in the example of comparison 1 example 1 investigated the pulse discharge property in cellular-phone mode as a power supply [as opposed to / only using the square shape rechargeable lithium-ion battery of 850mAh(s) / the hybrid element of the above-mentioned example 1 in theoretical electric capacity] for comparison.

[0020] That is, it discharged by -10 degrees C by the load in cellular-phone mode (it is the repeat of 4.0msec(s) at 0.5msec(s) and 0.1A in 1.5A), using respectively the hybrid element of the above-mentioned example 1, and the cell of the example 1 of comparison as a power supply, and the pulse discharge property shown in drawing 3 was acquired.

[0021] When it is used for a cellular phone and uses only the cell of the example 1 of comparison as a power supply to the ability to operate for 75 minutes, if the place where the minimum voltage of a pulse load became 2.75V is electric discharge termination

as shown in drawing 3, when using the hybrid element of an example 1 as a power supply, a charging time value is 75 minutes, and a charging time value is 58 minutes, and when it is used for a cellular phone, it turns out that it can operate only for 58 minutes.

[0022] The electric double layer capacitor whose size of contents portions, such as a positive electrode and a negative electrode, is 40mmx45mm was produced using the sheathing material which laminated hot melt adhesive partially by 0.1mm in example 2 thickness in one field of an aluminum plate whose dimension is 50mmx55mm. The composition in respect of [, such as a positive electrode of this electric double layer capacitor, a negative electrode, separator, and the electrolytic solution,] the quality of the material was the same as that of the case of the aforementioned example 1, and the above-mentioned hot melt adhesive used what was formed in the shape of [thin] a sheet by the denaturation polyolefine system, having pierced it in the shape of a frame.

[0023] An electric double layer capacitor is as being shown in drawing 4, separator 13 arranges between a positive electrode 11 and a negative electrode 12, the aluminum plate used as the aforementioned substrate is the collecting electrode plate 15 for negative electrodes, the lead object 17 was pulled out from one edge of a positive electrode 11, and the sheathing material 18 which consists of a laminate film of aluminum and plastics has covered the whole contents.

[0024] Since this electric double layer capacitor 1 formed the closure portion thinly using hot melt adhesive not using a frame like an example 1 as a closure member, its whole thickness was flexible at the shape of a sheet which is 1.2mm.

[0025] The electric double layer capacitor of the shape of this sheet was twisted around the periphery section of a 14650 form (cylindrical shape with outer-diameter [of 14mm], and a height of 65mm) rechargeable lithium-ion battery, and the lead object was connected, and the hybrid element shown in drawing 5 was produced. Winding to the periphery section of the rechargeable lithium-ion battery of the above-mentioned electric double layer capacitor was performed so that the free field of the charge collector 15 for negative electrodes of the electric double layer capacitor 1 might contact the peripheral wall of a cell 2 directly. The outer diameter (X) of a cell 2 is 14mm, and the thickness (1.2mm) of the above-mentioned electric double layer capacitor 1 is contained within the limits of $0.0025X-0.15X$ (0.035mm - 2.1mm) to the outer diameter (X= 14mm) of a cell 2.

[0026] If the hybrid element shown in drawing 5 is explained, 1 is an electric double layer capacitor and the hybrid element is formed by twisting this electric double layer capacitor 1 around the periphery section of a cell 2. Among this hybrid element, first, if a cell 2 is explained in detail, a positive electrode 21 makes a lithium-cobalt oxide an active material, and the negative electrode 22 makes the artificial graphite the active material, and these positive electrodes 21 and negative electrodes 22 are spirally wound through the separator 23 which consists of a microporosity polypropylene film, and are inserted in the cell case 25 as a spiral electrode object. However, in advance of insertion of the above-mentioned spiral electrode object, in the cell case 25, the insulator 26 which becomes the pars basilaris ossis occipitalis from a polytetrafluoroethylene sheet is arranged, and even if it meets the inner skin of the cell case 25, the insulator 27 which consists of a polytetrafluoroethylene is arranged. And in this cell case 25, it is LiPF6 to the mixed solvent of the volume ratio 1:1 of ethylene carbonate and ethyl methyl carbonate. The electrolytic solution 24 which comes to carry out 1 mol/l dissolution is poured in.

[0027] It is arranged at opening of the cell case 25, and the above-mentioned cell case 25 is a product made from stainless steel, and the heat variant-part material 31 is [it serves as the negative-electrode terminal and / the obturation board 28 is a product made from stainless steel, and / gas air hole 28a is prepared in the center section, and / the annular gasket 29 is a product made from polypropylene, and / flexible sheet metal 30 is a product made from titanium, and] a product made from polypropylene. and -- the terminal assembly 32 made from rolled steel -- a cutting edge, when 32a and gas discharge hole 32b were prepared, gas occurs, the internal pressure of a cell rises and flexible sheet metal 30 deforms into the interior of a cell by the internal pressure elevation the above -- a cutting edge -- flexible sheet metal 30 is destroyed by 32a, and the gas inside a cell is discharged from above-mentioned gas discharge hole 32b to the cell exterior, and it is designed so that the destruction under the high pressure of a cell can be prevented And the annular insulating packing 33 is arranged between the cell case 25 and the obturation board 28, a positive electrode 21 and the obturation board 28 are electrically connected by the lead object 34 made from aluminum, and the lead object 35 connects electrically between the negative electrode 22 and the cell case 25.

[0028] Although the electric double layer capacitor 1 is twisted around the periphery section of the above-mentioned cell 2 and the hybrid element is formed of it, in this drawing 5, the detail of the internal configuration of the electric double layer capacitor 1 is not shown, but shows the whole by A. However, a required member is shown about a sheathing portion, the collecting electrode plate 15 for negative electrodes contacts the peripheral wall of the cell case 25 of a cell 2 directly, and in the periphery section, it pastes up with hot melt adhesive 19, and, as for this collecting electrode plate 15 for negative electrodes and sheathing material 18, it makes sealing structure the interior of the electric double layer capacitor 1. And it connects with the head of the terminal assembly 32 used as the positive-electrode terminal of a cell 2, and the electric double layer capacitor 1 and a cell 2 can connect now electrically the other end of the lead object 17 (refer to drawing 4) which connected the end to the positive electrode 11 of the electric double layer capacitor 1 by contacting directly the peripheral wall of the cell case 25 where it and the collecting electrode plate 15 for negative electrodes constitute the negative-electrode terminal of a cell 2. Although the end of the above-mentioned lead object 17 arrived at the interior of the electric double layer capacitor 1 and is connected with the positive electrode 11, since the internal configuration of an electric double layer capacitor is not shown in detail, illustration of the lead object 17 has been carried out by this drawing 5 only till the place of the hot melt adhesive 19 for closure.

[0029] The pulse discharge property in cellular-phone mode was investigated so that it considered as a power supply after charging the above-mentioned hybrid element completely, and it might be shown after that, using as the power supply for comparison the cell shown in the after-mentioned example 2 of comparison.

[0030] The pulse discharge property in cellular-phone mode was investigated only using the 14650 form rechargeable lithium-ion

battery used in the example of comparison 2 example 2, and the same rechargeable lithium-ion battery as a power supply for comparison to the hybrid element of the above-mentioned example 2.

[0031] That is, it discharged by -10 degrees C like the example 1 by the load in cellular-phone mode (it is the repeat of 4.0msec(s) at 0.5msec(s) and 0.1A in 1.5A), using the hybrid element of the above-mentioned example 2, and the cell of the example 2 of comparison as a power supply, and the pulse discharge property shown in drawing 6 was acquired, respectively.

[0032] When it is used for a cellular phone and uses only the cell of the example 2 of comparison as a power supply to the ability to operate for 60 minutes, if the place where the minimum voltage of a pulse load became 2.75V is electric discharge termination as shown in drawing 6, when using the hybrid element of an example 2 as a power supply, a charging time value is 60 minutes, and a charging time value is 40 minutes, and when cellular-phone use is carried out, it turns out that it can operate only for 40 minutes.

[0033] The hybrid element which twists around ER17 / 50 form (cylindrical shape with outer-diameter [of 17mm] and a height of 50mm) thionyl chloride-lithium cell the electric double layer capacitor shown in drawing 4 used in the example 3 example 2 and the same electric double layer capacitor, and is shown in drawing 7 and drawing 8 was produced. The outer diameter (X) of the above-mentioned cell 2 is 17mm, and since the thickness of the electric double layer capacitor 1 is 1.2mm like the case of the aforementioned example 2, the thickness (1.2mm) of this electric double layer capacitor 1 is contained within the limits of 0.0025X-0.15X (0.0425mm - 2.55mm) to the outer diameter (X= 17mm) of a cell 2.

[0034] If the hybrid element shown in drawing 7 is explained, although the hybrid element is produced by twisting the electric double layer capacitor 1 around the periphery section of a cell 2 Since the composition of the electric double layer capacitor 1 is the same as that of the case of an example 2 If the explanation is omitted and a cell 2 is explained in detail, a positive electrode 41 will consist of a carbon porosity Plastic solid. It consists of lithiums, one field of a negative electrode 42 stands face to face against a positive electrode 41 through the separator 43 which consists of a glass fiber nonwoven fabric, and the negative electrode 42 is stuck to the field of another side of a negative electrode 42 by the inner skin of the cell case 45.

[0035] The electrolytic solution 44 became a thionyl chloride from what carried out the 1.2 mol/l dissolution of the aluminum tetrachloride lithium, and the thionyl chloride which constitutes the above-mentioned electrolytic-solution solvent serves as the positive active material. It is stainless steel, the soffit section is sharp in the shape of a nail, the positive-electrode charge collector 46 is inserted into a positive electrode 41, and the upper-limit section is welded with the metallic pipe prepared in the cell lid 47, and constitutes the positive-electrode terminal 50.

[0036] The cell lid 47 has the so-called hermetic-sealing structure, and the glass layer 49 is formed in the inner circumference side of the body part 48 of being annular and the product made from stainless steel as an insulating layer. The metallic pipe used as an electrolytic-solution inlet at the time of cell assembly is prepared in the inner circumference side of the glass layer 49. The upper-limit section of the positive-electrode charge collector 46 is inserted in the metallic pipe, the upper-limit section of a metallic pipe and the positive-electrode charge collector 46 is welded in the state, the positive-electrode terminal 50 is constituted, and the periphery section of a body part 48 is welded with the inner circumference section of the opening edge of the cell case 45, and makes the interior of a cell sealing structure. And on the pars-basilaris-ossis-occipitalis inside of the cell case 45, the pars-basilaris-ossis-occipitalis insulating material 51 is arranged, the up insulating material 52 is arranged in the upper part of a positive electrode 41, and the resin layer 53 for an insulation is formed in the body 48 of the cell lid 47, and the upper part of the glass layer 49. And the other end of the lead object 17 which connected the end to the positive electrode 11 of the electric double layer capacitor 1 is connected to the positive-electrode terminal 50 of a cell 2, and the electric double layer capacitor 1 and the cell 2 are electrically connected by being directly in contact with the peripheral wall of the cell case 45 where the collecting electrode plate 15 for negative electrodes of it and the electric double layer capacitor 1 constitutes the negative-electrode terminal of a cell 2. Although the end of the above-mentioned lead object 17 arrived at the interior of the electric double layer capacitor 1 and is connected with the positive electrode 11, since this drawing 7 does not show the internal configuration of an electric double layer capacitor in detail, either, illustration of the lead object 17 has been carried out like the case of drawing 5 only till the place of the hot melt adhesive 19 for closure.

[0037] After having used the above-mentioned hybrid element as the power supply, and carrying out a long term storage at 60 degrees C after a partial discharge so that it may be shown after that, using as the power supply for comparison the cell shown in the after-mentioned example 3 of comparison, it discharged by constant resistance and the electric discharge property was investigated.

[0038] Only using ER17 / 50 form thionyl chloride-lithium cell used in the example of comparison 3 example 3, and the same thionyl chloride-lithium cell, it discharged like the above-mentioned example 3 as a power supply for comparison to the hybrid element of the above-mentioned example 3, and the electric discharge property was investigated.

[0039] That is, after storing for 12 days at 60 degrees C after 30% partial discharge, using the hybrid element of the above-mentioned example 3, and the cell of the example 3 of comparison as a power supply, it discharged by 220-ohm constant resistance, and the electric discharge property shown in drawing 9 was acquired, respectively.

[0040] As shown in drawing 9, the example 3 had few voltage drops at the time of discharge starting compared with the example 3 of comparison, and it turns out that the electric discharge property when carrying out a long term storage can be improved, and an effect is also to pulse load usage after a partial discharge.

[0041]

[Effect of the Invention] As explained above, according to this invention, it was able to consider as the power supply with good pulse discharge property, especially pulse discharge property in low temperature by using an electric double layer capacitor and a

cell as a hybrid element. Moreover, there was also an advantage that handling became easy, by having unified each.

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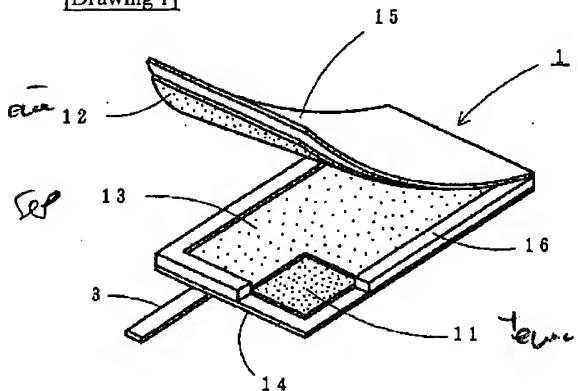
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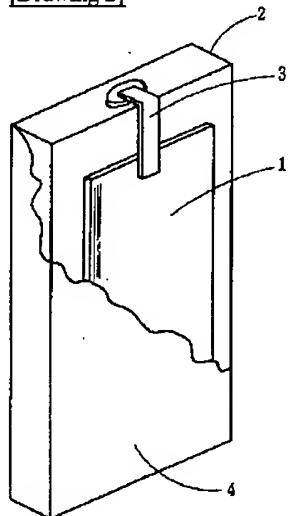
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DRAWINGS

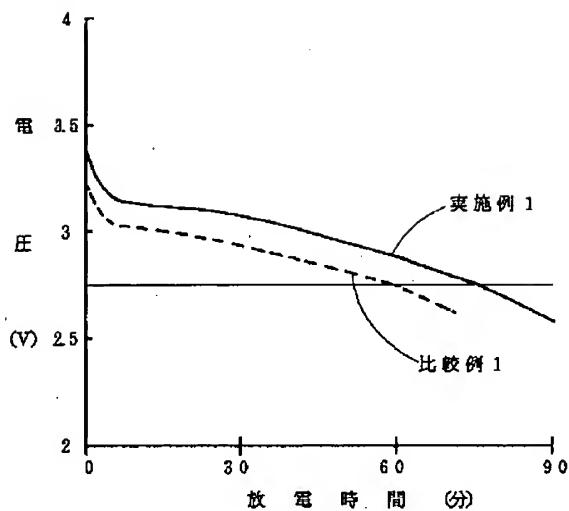
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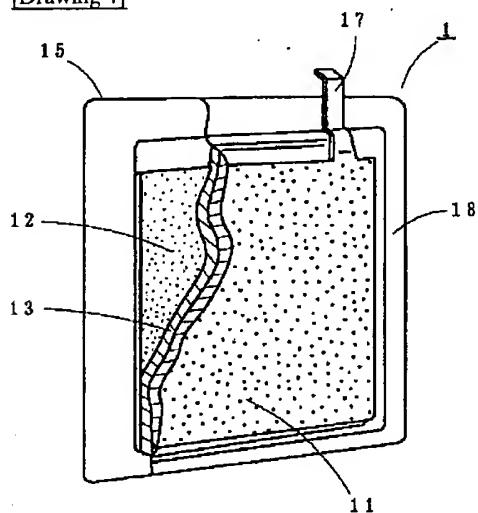
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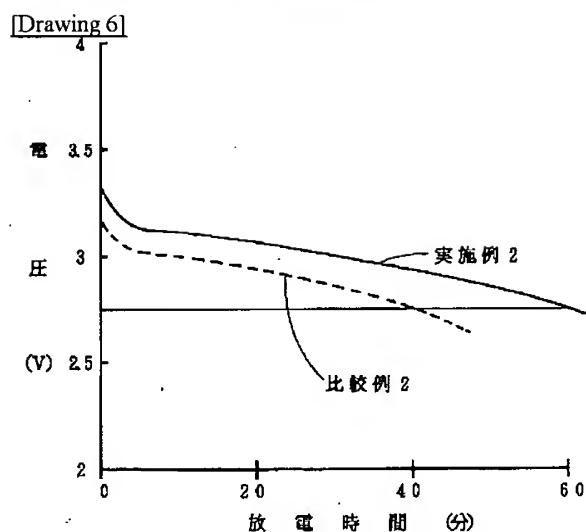
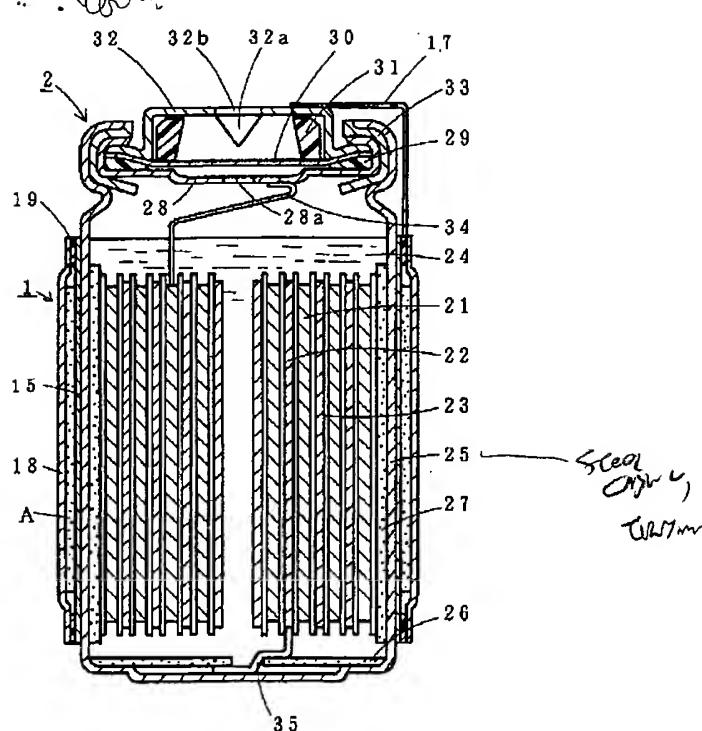


[Drawing 3]

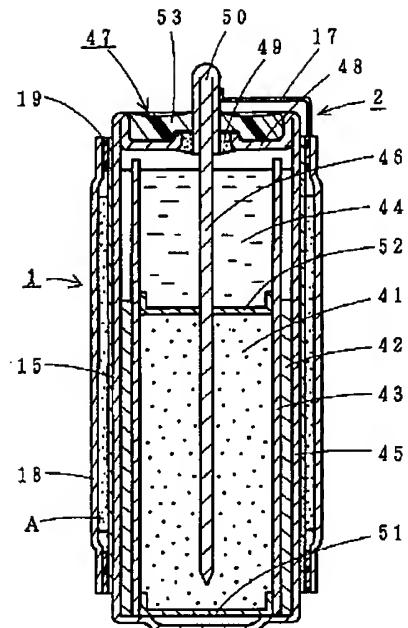


[Drawing 4]

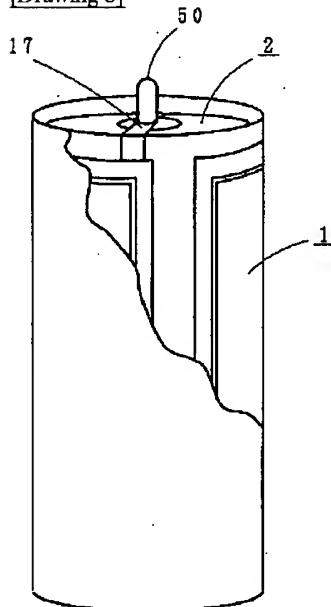




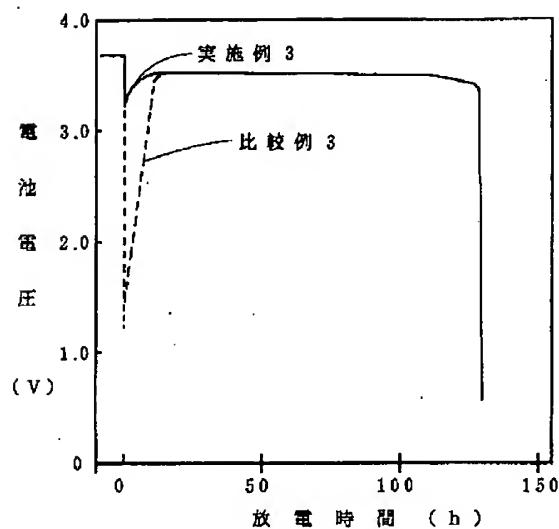
[Drawing 7]



[Drawing 8]



[Drawing 9]



[Translation done.]